

## REMARKS

Claims 1, 2, 10, 18, 19, 21, 22 23 and 25 have been amended. Claims 6, 20 and 24 have been canceled. Claims 27-29 have been added. Claims 1-5, 7-19, 21-23 and 25-29 are pending. The amendment in the claims is supported in the application at page 3, lines 26-31, page 9, lines 1-31, page 11 line 14 through page 12 line 7 and FIGS. 3-4.

In the Office Action dated November 5, 2002 ("Office Action"), claims 1-11 and 18-26 were rejected under 35 U.S.C. 112. Claims 1, 18 and 22 claims, as amended, avoid these rejections, because they no longer recite "sufficient amount," "desired properties" or "sufficiently." The dependent claims similarly avoid the rejection based on the amendments to claims 1, 18 and 22.

Claims 1-11 and 18-26 were "rejected under 35 U.S.C. 103(a) as being unpatentable over Watanabe et al. (U.S. 5,929,133) in view of Dehennau et al. (U.S. 4,774,146.)." Office Action at page 3. The application respectfully argues that the Examiner has failed to prove a prima facie case of obviousness because there is no motivation to combine these two references. In fact, one of skill in the art would understand that these two references teach away from each other. "If proposed modification would render the prior art invention being modified unsatisfactory for its intended purpose then there is no suggestion or motivation to make the proposed modification." MPEP 2143.01.

The Examiner stated that "Watanabe and Dehennau are analogous art because they are from the same field of films." Office Action at page 4. Dehennau is directed exclusively to structures comprising a layer of polyvinylidene chloride copolymer attached to a layer of polyvinyl chloride (PVC) through an adhesive. In particular, Dehennau discloses solving the problem of securely bonding together layers of polyvinylidene chloride and polyvinyl chloride.

As stated in Dehennau, “[t]he invention thus lies essentially in the use of a mixture of polymeric adhesives consisting of 10 to 90 parts by weight of a copolymer of vinyl acetate and ethylene and of 90 to 10 parts by weight of a copolymer of vinyl chloride and vinyl acetate ... for ***bonding and producing adhesion*** of a layer of vinylidene chloride copolymer to a layer of plasticized vinyl chloride polymer.” Col 2, lines 11-19 (emphasis added). Thus, the invention of Dehennau is improved bonding of vinylidene chloride layer to polyvinyl chloride through an adhesive.

As disclosed by Dehennau, “[i]t is well known to improve the ***gas and vapour imperviousness*** of various packages of made of bulk thermoplastic polymers by combining them with a vinylidene chloride copolymer....” Col 1, lines 15-18 (emphasis added). As stated in the Concise Encyclopedia of Chemical Technology at page 2078-79, vinylidene chloride-vinyl chloride copolymers are used in “[r]igid containers for food packaging” and may be used for coatings. “The principle applications for these materials are as barrier coatings on paper products and, more recently, on plastic films.” A copy of pages 2076-79 of the Concise Encyclopedia of Chemical Technology is enclosed.

In contrast, Watanabe discloses that PVC food wrapping requires air permeability, a property that would be destroyed if the film of Dennehou is combined with the film of Watanabe.

Watanabe discloses the following:

PVC food packaging wrap has been increasingly widely used for packaging fresh food as the importance of supermarkets in the retail business grows. The use of PVC food packaging wrap in homes has also increased with the increase in the use of refrigerators and microwave ovens for preserving and cooking food. The PVC food packaging wrap for such applications are required to have a clinging property for the convenience of wrapping food items, ***a freshness preserving property based on a suitable degree of air permeability***, an anti-fogging property, and transparency.”

Col. 1, lines 13-24 (emphasis added).

Since Dehennau discloses the use of PVC only as a coating layer for polyvinylidene chloride copolymer and a polyvinylidene chloride copolymer layer would destroy the function of the film of Watanabe, there is no motivation to combine the two references.

The Examiner further supported an obviousness rejection by stating that “[i]t would have been obvious to one of ordinary skill in the art to include an additional layer(s) consisting of polyvinyl chloride to the packaging film of Watanabe because Dehennau teaches the additional layers helps maintain the integrity of the film surface, by avoiding folds and small cracks (column 2, lines 9-10).” Office Action at page 4. However, Dehennau teaches that this problem occurs when a copolymer of vinyl chloride and acetate is used to bond PVC to vinylidene chloride copolymer and the resulting laminate is exposed to heat. Dehennau discloses a prior art example in which polyvinylidene chloride copolymer is bonded to a PVC layer. In this example, adhesion between the layers was weak or nonexistent and cracks appeared on the surface after heat treatment. Col. 1, lines 23-37. Since Watanabe discloses a single layer film of solely PVC, not a laminate of PVC and vinylidene chloride copolymer, there is no indication that the films of Watanabe would form the same cracks and folds as the prior art disclosed in Dehennau. Thus there is no motivation to combine the solution of Dehennau with the film of Watanabe, because there is no problem of cracks and folds disclosed in Watanabe.

The Examiner further stated that “Dehennau additionally teaches a coating layer of polyvinyl chloride (column 2, lines 67-68).” Office Action at page 4. However, Dehennau teaches, not a coating film layer of PVC, but the use of PVC as a coating for polymers of vinyl acetate and ethylene to moderate the tackiness of the polymers. Col. 2, lines 56-60. Dehennau teaches that such a coating may be created “by the addition of a thermoplastic polymer latex to a vinyl acetate polymer latex and coagulation of the whole, for example by the addition of an

electrolyte.” Col. 3, lines 5-8. Thus, Dehennau teaches blending PVC into polymers of vinyl acetate and ethylene, not forming separate structural layer of PVC. As further indication that PVC is not used as a separate structural layer, Dehennau discloses that the “thermoplastic coating polymer is generally present in a proportion of at most approximately 10% by weight of the coated acetate polymer.” Col. 2 lines 68- col. 3 line 3. Since Watanabe discloses a single layer film without an adhesive layer, there is no need to reduce the tackiness of a polymer of vinyl acetate and ethylene and thus no motivation to combine this teaching of Dehennau with the teachings of Watanabe.

In addition, the claims, as amended, clarify the differences between the claimed film and the disclosures of Dehennau and Watanabe. The multiple PVC layers disclosed by Dehennau are separated by a barrier layer of polyvinylidene chloride and adhered to the polyvinylidene chloride layer with an adhesive layer. Dehennau, col. 2, lines 20-37. The claims as amended recite that the film comprises “at least two layers, each layer comprising polyvinyl chloride and plasticizer” and that the “two polyvinyl chloride layers are adjacent to one another.” In contrast, the film of Watanabe is a single layer film and the structure of Dehennau is a multiple layer film with a polyvinylidene barrier layer and two adhesive layers between any plasticized polyvinyl chloride layers.

In conclusion, based on the teachings of Dehennau (requiring a polyvinylidene barrier layer) and Watanabe (requiring air permeability), the two references cannot be combined without destroying the functionality of the disclosed films. Therefore, there is no motivation to combine the two references and the Examiner has failed to establish a prima facie case of obviousness. In addition, the claims, as amended, further distinguish the claimed film from the recited references. Since the independent claims, claims 1, 11 and 22 are believed to be in patentable form, the

claims depending from the independent claims also believed to be patentable over Watanabe and Dehennau.

Accordingly, Applicant believes that the application is now in condition for immediate allowance. In the event the Examiner finds any remaining impediment to a prompt allowance of the claims which could be clarified or satisfied by a telephonic discussion or interview, the Examiner is respectfully requested to initiate the same with the undersigned attorney.

DATED this 5 day of May 2003.

Respectfully submitted,



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**MARKED-UP VERSION SHOWING THE CHANGES MADE IN THE CLAIMS**

1. (Twice Amended) A packaging film comprising:  
  
at least two layers, wherein [that] each layer comprises [include] polyvinyl chloride and plasticizer [at least one other constituent], [included in sufficient amount so that the layers have desired properties], and  
  
wherein the at least two polyvinyl chloride layers are adjacent to one another.
  
2. (Twice amended) The film of claim 1, wherein each layer further comprises [the constituent] a surface active agent.
  
10. (Twice amended) The film of claim 1, wherein at least one of the layers further comprises [the constituent is] a copolymer.
  
18. (Once Amended) A packaging film comprising:  
  
at least two layers, wherein [that] each layer comprises [include] polyvinyl chloride and plasticizer, [at least one other constituent included in sufficient amount so that the layers have desired properties]  
  
wherein the at least two layers are adjacent to one another, and  
  
wherein the film has a total thickness of up to 2 mil [at least two layers are sufficiently distinct from each other to have different gas permeabilities].
  
19. (Once Amended) The film of claim 18, wherein at least one of the layers further comprises [the constituent is] a surface active agent.

21. (Once Amended) The film of claim 18, wherein at least one of the layers further comprises [the constituent is] a copolymer.

22. (Once Amended) A packaging film comprising:

at least two layers, wherein [that] each layer comprises [include] polyvinyl chloride and plasticizer, [at least one other constituent included in sufficient amount so that the layers have desired properties]

wherein the at least two layers are adjacent to one another; and

wherein the at least two layers are sufficiently distinct from each other to have different melting points.

19. (Twice Amended) The film of claim 22, wherein at least one of the layers further comprises [the constituent is] a surface active agent.

21. (Once Amended) The film of claim 22, wherein at least one of the layers further comprises [the constituent is] a copolymer.

27. (New) The film of claim 1, wherein the film has a thickness ranging no more than about 1 mil.

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28. (New) The film of claim 1 wherein the at least two layers are sufficiently distinct from each other to have different gas permeabilities.

29. (New) the film of claim 18 wherein the at least two layers are sufficiently distinct from each other to have different gas permeabilities.

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# CONCISE ENCYCLOPEDIA OF CHEMICAL TECHNOLOGY

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4th EDITION



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John Wiley & Sons, Inc.

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there is economic justification, these streams can be fractionated to recover specific, useful components, and the remainder subsequently incinerated and scrubbed to remove HCl. Alternative methods include catalytic oxidation or combustion, and may involve recycle of HCl to oxychlorination and recovery of the heat of combustion to make high pressure steam. Process water streams from vinyl chloride manufacture are typically steam-stripped to remove volatile organics, neutralized, and then treated in a conventional wastewater treatment process. Solid by-products include sludge from wastewater treatment, spent catalyst, and coke from the EDC pyrolysis process. These need to be disposed of in an environmentally sound manner, eg, by sludge digestion, incineration, landfill, etc.

#### Environmental Considerations

Since the early 1980s, there has been much debate among environmental activist organizations, industry, and government about the impact of chlorine chemistry on the environment. One aspect of this debate involves the incidental manufacture and release of trace amounts of hazardous compounds such as polychlorinated dibenzodioxins, dibenzofurans, and biphenyls (PCDDs, PCDFs, and PCBs, respectively, but often referred to collectively as dioxins) during the production of chlorinated compounds like vinyl chloride. In 1994, the EPA released a review draft of its reassessment of the impact of dioxins in the environment on human health, which prompted speculation as to the amount of dioxins that might be attributed to chlorine-based industrial processes. The U.S. vinyl industry responded by committing to a voluntary characterization of dioxin levels in its products and in emissions from its facilities to the environment. The results of this study to date support the vinyl industry's position that it is a minor source of dioxins in the environment. In addition, a global benchmark study released recently by the American Society of Mechanical Engineers found no relationship between the chlorine content of waste and dioxin emissions from combustion processes.

Because of the toxicity of vinyl chloride, the EPA in 1975 proposed emission standards for vinyl chloride manufacture. This proposal was subsequently enacted as EPA Regulation 40 CFR 61, Subpart F. Compliance testing began in 1978. Environmental concerns and government regulations have prompted a major increase in the amount of add-on technology used in U.S. vinyl chloride production plants.

#### Technology Trends

The ethylene-based, balanced vinyl chloride process, which accounts for nearly all capacity worldwide, has been practiced by a variety of vinyl chloride producers since the mid-1950s. The technology is mature, so that the probability of significant changes is low. New developments in production technology will likely be based on incremental improvements in raw material and energy efficiency, environmental impact, safety, and process reliability.

More recent trends include widespread implementation of oxygen-based oxychlorination, further development of new catalyst formulations, a broader range of energy recovery applications, a continuing search for ways to improve conversion and minimize by-product formation during EDC pyrolysis, and chlorine source flexibility. The application of computer model-based process control and optimization is growing as a way to achieve even higher levels of feedstock and energy efficiency and plant process reliability.

#### Health and Safety Factors

Vinyl chloride is an OSHA-regulated substance. Current OSHA regulations impose a permissible exposure limit (PEL) to vinyl chloride vapors of no more than 1.0 ppm averaged over any 8-h period. Short-term exposure is limited to 5.0 ppm averaged over any 15-min period. Wherever exposure is above the OSHA limit, respirators are required. Contact with liquid vinyl chloride is prohibited.

Chronic exposure to vinyl chloride at concentrations of 100 ppm or more is reported to have produced Raynaud's syndrome, lysis of the

distal bones of the fingers, and a fibrosing dermatitis. However, these effects are probably related to continuous intimate contact with the skin. Chronic exposure to large amounts of vinyl chloride gas over a period of many years is also reported to have produced a rare cancer of the liver (angiosarcoma) in a small number of workers.

Vinyl chloride also poses a significant fire and explosion hazard. It has a wide flammability range, from 3.6% to 33.0% by volume in air. Large fires of the compound are very difficult to extinguish, while vapors represent a severe explosion hazard.

Vinyl chloride is generally transported via pipeline, and in railroad tank cars and tanker ships. Because hazardous peroxides can form on standing in air, especially in the presence of iron impurities, vinyl chloride should always be handled and transported under an inert atmosphere.

#### Uses

Vinyl chloride has gained worldwide importance because of its industrial use as the precursor to PVC. It is also used in a wide variety of copolymers. The inherent flame-retardant properties, wide range of plasticized compounds, and low cost of polymers from vinyl chloride have made it a significant industrial chemical. About 95% of current vinyl chloride production worldwide ends up in polymer or copolymer applications. Vinyl chloride also serves as a starting material for the synthesis of a variety of industrial compounds. The primary nonpolymeric uses of vinyl chloride are in the manufacture of vinylidene chloride and tri- and tetrachloroethylene.

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**VINYL ETHER.** See ANESTHETICS; VINYL POLYMERS.

**VINYL FIBERS.** See FIBERS, POLY(VINYL ALCOHOL).

#### VINYLIDENE CHLORIDE MONOMER AND POLYMERS

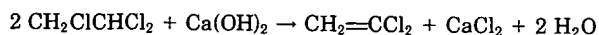
Vinylidene chloride copolymers' most valuable property is low permeability to a wide range of gases and vapors. From the beginning in 1939, the word Saran has been used for polymers with high vinylidene chloride content, and it is still a trademark of The Dow Chemical Company in some countries. Sometimes Saran and poly(vinylidene chloride) are used interchangeably in the literature.

Three types of comonomers are commercially important: vinyl chloride; acrylates, including alkyl acrylates and alkylmethacrylates; and acrylonitrile. When extrusion is the method of fabrication, the formulation includes plasticizers, stabilizers, and extrusion aids.

#### Monomer

**Properties.** Pure vinylidene chloride (1,1-dichloroethylene) is a colorless, mobile liquid with a characteristic sweet odor. Its properties are summarized in Table 1. Vinylidene chloride is soluble in most polar and nonpolar organic solvents. Its solubility in water (0.25 wt %) is nearly independent of temperature at 16-90°C.

**Manufacture.** Vinylidene chloride monomer can be conveniently prepared in the laboratory by the reaction of 1,1,2-trichloroethane with aqueous alkali:



Vinylidene chloride (VDC) is prepared commercially by the dehydrochlorination of 1,1,2-trichloroethane with lime or caustic in slight excess (2–10%). A continuous liquid-phase reaction at 98–99°C yields ~90% VDC. Commercial grades contain 200 ppm of the monomethyl ether of hydroquinone (MEHQ).

For many polymerizations, MEHQ need not be removed; instead, polymerization initiators are added. Vinylidene chloride from which the inhibitor has been removed should be refrigerated in the dark at –10°C, under a nitrogen atmosphere, and in a nickel-lined or baked phenolic-lined storage tank. If not used within one day, it should be reinhibited.

**Health and Safety Factors.** Vinylidene chloride is highly volatile and, when free of decomposition products, has a mild, sweet odor. A single, brief exposure to a high concentration of vinylidene chloride vapor, eg, 2000 ppm, rapidly causes intoxication, which may progress to unconsciousness on prolonged exposure. Vinylidene chloride is hepatotoxic, but does not appear to be a carcinogen. The liquid is irritating to the skin after only a few minutes of contact. In the presence of air or oxygen, uninhibited vinylidene chloride forms a violently explosive complex peroxide at temperatures as low as 40°C. Vinylidene chloride containing peroxides may be purified by being washed several times, either with 10 wt % sodium hydroxide at 25°C or with a fresh 5 wt % sodium bisulfite solution.

Table 1. Properties of Vinylidene Chloride Monomer

Property	Value
odor	pleasant, sweet
color (APHA)	0–10
sol of monomer in H <sub>2</sub> O at 25°C, wt %	0.25
sol of H <sub>2</sub> O in monomer at 25°C, wt %	0.035
normal bp, °C	31.56
fp, °C	–122.56
flash point, °C	
Tag closed cup	–28
Tag open cup	–16
flammable limits in air (ambient conditions), vol %	6.5–15.5
autoignition temp, °C	513 <sup>a</sup>
latent $\Delta H_v$ , kJ/mol <sup>b</sup>	
at 25°C	26.48 ± 0.08
at normal bp	26.14 ± 0.08
latent $\Delta H_m$ fp, J/mol <sup>b</sup>	6514 ± 8
at 25°C, $\Delta H_p$ , kJ/mol <sup>b</sup>	–75.3 ± 3.8
$\Delta H_c$ , liquid monomer at 25°C, kJ/mol <sup>b</sup>	1095.9
$\Delta H_f$ , at 25°C, kJ/mol <sup>b</sup>	
liquid monomer	–25.1 ± 1.3
gaseous monomer	1.26 ± 1.26
$C_p$ , at 25°C, J/(mol·K) <sup>b</sup>	
liquid monomer	111.27
gaseous monomer	67.03
$T_c$ , °C	220.8
$P_c$ , MPa <sup>c</sup>	5.21
$V_c$ , cm <sup>3</sup> /mol	218
liquid density, at 20°C, g/cm <sup>3</sup>	1.2137
index of refraction at 20°C, $n_D$	1.42468
absolute viscosity at 20°C, mPa·s (= cP)	0.3302 <sup>d</sup>

<sup>a</sup> Inhibited with methyl ether of hydroquinone.

<sup>b</sup> To convert J to cal, divide by 4.184.

<sup>c</sup> To convert MPa to atm, divide by 0.101.

<sup>d</sup>  $P$  measured from 6.7–104.7 kPa. To convert kPa to mm Hg, multiply by 7.5 (add 0.875 to the constant to convert  $\log_{10}$  to  $\log_{10}$   $\eta_r$ ).

## Polymerization

**Homopolymerization.** The free-radical polymerization of VDC has been carried out by solution, slurry, suspension, and emulsion methods. Slurry polymerizations are usually used only in the laboratory. The heterogeneity of the reaction makes stirring and heat transfer difficult; consequently, these reactions cannot be easily controlled on a large scale. Aqueous emulsion or suspension reactions are preferred for large-scale operations. The spontaneous polymerization of VDC, so often observed when the monomer is stored at room temperature, is caused by peroxides formed from the reaction of VDC with oxygen. Very pure monomer does not polymerize under these conditions. Heterogeneous polymerization is characteristic of a number of monomers, including vinyl chloride and acrylonitrile.

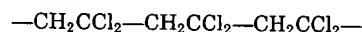
Emulsion and suspension reactions are doubly heterogeneous; the polymer is insoluble in the monomer and both are insoluble in water.

The instability of PVDC is one of the reasons why ionic initiation of VDC polymerization has not been used extensively. Many of the common catalysts either react with the polymer or catalyze its degradation.

**Copolymerization.** The importance of VDC as a monomer results from its ability to copolymerize with other vinyl monomers. Bulk copolymerizations yielding high VDC-content copolymers are normally heterogeneous. During copolymerization, one monomer may add to the copolymer more rapidly than the other. Batch reactions carried to completion usually yield polymers of broad composition distribution. More often than not, this is an undesirable result.

## Polymer Structure and Properties

The chemical composition of poly(vinylidene chloride) has been confirmed by various techniques, including elemental analysis, x-ray diffraction analysis, degradation studies, and ir, Raman, and nmr spectroscopy. The polymer chain is made up of vinylidene chloride units added head-to-tail:



Molecular weights of PVDC can be determined directly by dilute solution measurements in good solvents. Viscosity studies indicate that polymers having degrees of polymerization from 100 to more than 10,000 are easily obtained. Dimers and polymers having DP < 100 can be prepared by special procedures.

The crystal structure of PVDC is fairly well established. Several unit cells have been proposed. The unit cell contains four monomer units with two monomer units per repeat distance. The calculated density, 1.96 g/cm<sup>3</sup>, is higher than the experimental values, which are 1.80–1.94 g/cm<sup>3</sup> at 25°C, depending on the sample. The melting temperature,  $T_m$ , of PVDC is independent of molecular weight above DP = 100. The properties of PVDC (Table 2) are usually modified by copolymerization.

The highly crystalline particles of PVDC precipitated during polymerization are aggregates of thin lamellar crystals.

Melting temperatures of as-polymerized powders are high, ie, 198–205°C. As-polymerized PVDC does not have a well-defined glass-transition temperature because of its high crystallinity. The amorphous polymer has a glass-transition temperature of –17°C. Once melted, PVDC does not regain its as-polymerized morphology when subsequently crystallized.

Poly(vinylidene chloride) does not dissolve in most common solvents at ambient temperatures. Copolymers, particularly those of low crystallinity, are much more soluble. However, one of the outstanding characteristics of vinylidene chloride polymers is resistance to a wide range of solvents and chemical reagents. The insolubility of PVDC results less from its polarity than from its high melting temperature. It dissolves readily in a wide variety of solvents above 130°C.

Poly(vinylidene chloride) also dissolves readily in certain solvent mixtures. One component must be a sulfoxide or *N,N*-dialkylamide. Effective cosolvents are less polar and have cyclic structures.

**Mechanical Properties.** Because PVDC is difficult to fabricate into suitable test specimens, very few direct measurements of its mechanical properties have been made. Some characteristic properties of high

Table 2. Properties of Poly(vinylidene chloride)

Property	Best value	Reported values
$T_m$ , °C	202	198–205
$T_g$ , °C	-17	-19 to -11
density at 25°C, g/cm <sup>3</sup>		
amorphous	1.775	1.67–1.775
unit cell	1.96	1.949–1.96
crystalline		1.80–1.97
refractive index (crystalline), $n_D$	1.63	
$\Delta H_m$ , J/mol <sup>a</sup>	6275	4600–7950

<sup>a</sup> To convert J to cal, divide by 4.184.

VDC content, unplasticized copolymers are listed in Table 3. The performance of a given specimen is sensitive to morphology, including the amount and kind of crystallinity, as well as orientation. Tensile strength increases with crystallinity, whereas toughness and elongation decrease. Orientation, however, improves all three properties.

In cases where the copolymers have substantially lower glass-transition temperatures, the modulus decreases with increasing comonomer content.

The long side chains of the acrylate ester group can apparently act as internal plasticizers. Substitution of a carboxyl group on the polymer chain increases brittleness. Copolymers of VDC with *N*-alkylacrylamides are more brittle than the corresponding acrylates even when the side chains are long.

Vinylidene chloride polymers are more impermeable to a wider variety of gases and liquids than other polymers. For example, commercial copolymers are available with oxygen permeabilities of 0.05 nmol/m<sup>2</sup>·s·GPa. This is a consequence of the combination of high density and high crystallinity in the polymer. An increase in either tends to reduce permeability. Permeability is affected by the kind and amounts of comonomer as well as crystallinity. A more polar comonomer, eg, an AN comonomer, increases the water-vapor transmission more than VC when other factors are constant. All VDC copolymers, are very impermeable to aliphatic hydrocarbons. Plasticizers increase permeability. However, water does not alter the permeability.

### Degradation Chemistry

Vinylidene chloride polymers are highly resistant to oxidation, permeation of small molecules, and biodegradation, which makes them extremely durable under most use conditions. However, these materials are thermally unstable and, when heated above about 120°C, undergo degradative dehydrochlorination.

The principal steps in the thermal degradation of VDC polymer are formation of a conjugated polyene sequence followed by carbonization.

On being heated, the polymer gradually changes color from yellow to brown and finally to black. In general, the stability of the

Table 3. Mechanical Properties of High Vinylidene Chloride Copolymers

Property	Range
tensile strength, MPa <sup>a</sup>	
unoriented	34.5–69.0
oriented	207–414
elongation, %	
unoriented	10–20
oriented	15–40
softening range (heat distortion), °C	100–150
flow temp, °C	>185
brittle temp, °C	-10 to 10
impact strength, J/m <sup>b</sup>	26.7–53.4

<sup>a</sup> To convert MPa to psi, multiply by 145.

<sup>b</sup> To convert J/m to ft-lbf/in., divide by 53.38 (see ASTM D256).

polymer reflects the method of preparation, with bulk > solution > suspension >> emulsion.

To some extent, the stability of VDC polymers is dependent on the nature of the comonomer present. Copolymers with acrylates degrade slowly. Copolymers with acrylonitrile or methacrylate undergo degradation more readily.

The degradation of VDC polymers in nonpolar solvents is comparable to degradation in the solid state. However, these polymers are unstable in many polar solvent. The rate of dehydrochlorination increases markedly with solvent polarity. This reaction is clearly unlike thermal degradation and may well involve the generation of ionic species as intermediates.

**Stabilization.** The ideal stabilizer system should (1) absorb or combine with evolved hydrogen chloride irreversibly under conditions of use, but not strip hydrogen chloride from the polymer chain; (2) act as a selective uv absorber; (3) contain a reactive dienophilic moiety capable of preventing discoloration by reacting with and disrupting the color-producing conjugated polymer sequences; (4) possess nucleophilicity sufficient for reaction with allylic dichloromethylene units; (5) possess antioxidant activity so as to prevent the formation of carbonyl groups and other chlorine-labilizing structures; (6) be able to scavenge chlorine atoms and other free radicals efficiently; and (7) chelate metals, eg, iron, to prevent chlorine coordination and the formation of metal chlorides.

### Commercial Methods of Polymerization and Processing

Emulsion polymerization and suspension polymerization are the preferred industrial processes. Either process is carried out in a closed, stirred reactor, which should be glass-lined and jacketed for heating and cooling. The reactor must be purged of oxygen, and the water and monomer must be free of metallic impurities to prevent an adverse effect on the thermal stability of the polymer.

Emulsion polymerization is used commercially to make vinylidene chloride copolymers. The principal advantages are high molecular weight polymers can be produced in reasonable reaction times, especially copolymers with vinyl chloride and monomer can be added during the polymerization to maintain copolymer composition control. The disadvantages of emulsion polymerization result from the relatively high concentration of additives in the recipe. The water-soluble initiators, activators, and surface-active agents generally cause the polymer to have greater water sensitivity, poorer electrical properties, and poorer heat and light stability.

Suspension polymerization of vinylidene chloride is used commercially to make molding and extrusion resins. The principal advantage is the use of fewer ingredients that might detract from the polymer properties. Stability is improved and water sensitivity is decreased. Extended reaction times and the difficult preparation of higher molecular weight polymers are disadvantages of the suspension process compared to the emulsion process, particularly for copolymers containing vinyl chloride.

The batch-suspension process does not compensate for composition drift, whereas constant-composition processes have been designed for emulsion or suspension reactions. It is more difficult to design controlled-composition processes by suspension methods.

### Applications

Vinylidene chloride–vinyl chloride copolymers were originally developed for thermoplastic molding applications, and small amounts are still used for this purpose. Extrusion of VDC–VC copolymers is the main fabrication technique for filaments, films, rods, and tubing or pipe, and involves the same concerns for thermal degradation, streamlined flow, and noncatalytic materials of construction as described for injection-molding resins. A significant application for vinylidene chloride copolymer resins is in the construction of multilayer film and sheet. This permits the design of a packaging material with a combination of properties not obtainable in any single material. Rigid containers for food packaging can be made from coextruded sheet that contains a layer of a barrier polymer.

Vinylidene chloride polymers have several properties that are valuable in the coatings industry: excellent resistance to gas and moisture vapor transmission, good resistance to attack by solvents and by fats and oils, high strength, and the ability to be heat-sealed.

Vinylidene chloride polymers are often made in emulsion, but usually are isolated, dried, and used as conventional resins. Stable latices have been prepared and can be used directly for coatings. The principal applications for these materials are as barrier coatings on paper products and, more recently, on plastic films.

Vinylidene chloride emulsion copolymers are used in a variety of ignition-resistant binding applications.

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**VINYLDENE POLYMERS, POLY(VINYLDENE FLUORIDE) ELASTOMERS.** See FLUORINE COMPOUNDS; ORGANIC.

Table 1. Physical Properties of Butvar Resins

Property	Method	B-72	B-74	B-76	B-90	B-98
mol mass $\times 10^3$ (avg)	<sup>a</sup>	170–250	120–250	90–120	70–100	40–70
viscosity 15 wt % Pa·s <sup>b</sup>	<sup>c</sup>	7–14	3–7	0.5–1	0.6–1.2	0.2–0.4
viscosity 10 wt % Pa·s <sup>b</sup>	<sup>d</sup>	1.6–2.5	0.8–1.3	0.2–0.45	0.2–0.4	0.07–0.2
Ostwald soln viscosity, mPa·s <sup>b</sup> (= cP)	<sup>e</sup>	170–260	40–50	18–28	13–17	6–9
specific gravity, 23°C/23°C	ASTM D792-50	1.100	1.100	1.083	1.100	1.100
refractive index	ASTM D542-50	1.490	1.490	1.485	1.490	1.490
vinyl alcohol content, wt %		17–20	17–20	11–13	18–20	18–20
vinyl acetate content, wt %		0–2.5	0–2.5	0–1.5	0–1.5	0–2.5

<sup>a</sup> Determined by size exclusion chromatography in tetrahydrofuran with low angle light scattering.

<sup>b</sup> To convert Pa·s to P, multiply by 10.

<sup>c</sup> Measured in 60:40 toluene:ethanol at 25°C using a Brookfield viscometer.

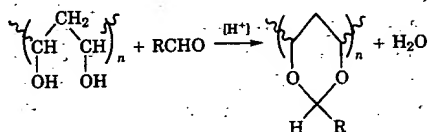
<sup>d</sup> Measured in 95% ethanol at 25°C using an Ostwald-Cannon-Fenske viscometer.

<sup>e</sup> B-72 in 7.5 wt % anhydrous methanol at 20°C; B-76 and B-79 in 5.0 wt % SD 29 ethanol at 25°C; B-74, B-90, and B-98 in 6.0 wt % anhydrous methanol at 20°C, all using an Ostwald-Cannon-Fenske viscometer.

## VINYL POLYMERS

### VINYL ACETAL POLYMERS

Vinyl acetal polymers are made by the acid-catalyzed acetalization of poly(vinyl alcohol) with aldehydes.



Although many members of this class of resins have been made, only poly(vinyl formal) (PVF) and poly(vinyl butyral) (PVB) are made in significant commercial quantities.

#### Synthesis and Structure

Poly(vinyl acetals) are made from poly(vinyl alcohol) and aldehydes by acid-catalyzed addition-dehydration. The degree of acetalization and the conditions used during the reaction significantly affect product properties. Batch and continuous processes in both aqueous and organic media are used during manufacturing. In single-stage batch processes, hydrolysis of poly(vinyl acetate) and acetalization of the poly(vinyl alcohol) hydrolysis product are carried out in the same kettle at the same time. In two-stage batch processes, hydrolysis and acetalization take place in separate kettles.

#### Physical Properties

Unformulated poly(vinyl acetal) resins form hard, unpliable materials which are difficult to process without using solvents or plasticizers. Plasticizers aid resin processing, lower the glass-transition temperature,  $T_g$ , and can profoundly change other physical properties of the resins.

Poly(vinyl acetals) can be formulated with other thermoplastic resins and with a variety of multifunctional cross-linkers. When cross-linking takes place the resin becomes thermoset. Thermosetting generally increases thermal stability, rigidity, and abrasion resistance, and improves resistance to solvents and to acids and bases. It also severely limits processability by making the resin insoluble and impossible to extrude.

#### Health and Safety Factors

Representative unformulated PVB and PVF resins are practically nontoxic orally (rats) and no more than slightly toxic after skin application (rabbits).

Some forms of these products may contain sufficient fines to be considered nuisance dust and present dust explosion potential if sufficient quantities are dispersed in air. Unformulated PVB and PVF resins have flash points above 370°C. The lower explosive limit (lel) for PVB dust in air is about 20 g/m<sup>3</sup>.

#### Poly(vinyl butyral)

Several grades are available that differ primarily in residual vinyl alcohol content and molecular weight. Both variables strongly affect solution viscosity, melt flow characteristics, and other physical properties. Some physical properties of various grades of Monsanto's Butvar resins are listed in Table 1. In general, resin melt and solution viscosity increase with increasing molecular weight and vinyl alcohol content, whereas the tensile strength of materials made from PVB increases with vinyl alcohol content for a given molecular weight.

Commercially available PVB resins are generally soluble in lower molecular weight alcohols, glycol ethers, and certain mixtures of polar and nonpolar solvents. A common solvent for all of the Butvar resins is a combination of 60 parts of toluene and 40 parts of ethanol (95%) by weight.

PVB resins are also compatible with a limited number of plasticizers and resins. Plasticizers (qv) improve processability, lower  $T_g$ , and increase flexibility and resiliency over a broad temperature range.